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MECHANICAL EFFECTS ON DIFFERENT SOLID TO LIQUID RATIO OF GEOPOLYMER FILLER IN EPOXY RESIN

Geopolymer is formed from the alkali activation of materials rich in Si and Al content with the addition of a silicate solution to enhance the properties of the materials. This paper presents research on the mechanical properties of fly ash-based geopolymer filler in epoxy resin by varying different solid to liquid ratios using sodium hydroxide and sodium silicate as the alkaline activator. However, the common problem observed from the solid to liquid ratio is the influence of curing time and compressive strength of geopolymer to have the best mechanical property. The mix design for geopolymers of solid to liquid ratio is essential in developing the geopolymer's mechanical strength. A series of epoxy filled with fly ash-based geopolymer materials with different solid to liquid ratio, which is prepared from 0.5 to 2.5 solid to liquid ratio of alkaline activator. The tensile strength and flexural strength of the epoxy filled with fly ash-based geopolymer materials is determined using Universal Testing Machine under tensile and flexural mode. It was found that the optimum solid to liquid ratio is 2.0, with the optimum tensile and flexural strength value. However, both the tensile and flexural properties of epoxy filled with fly ash-based geopolymer suddenly decrease at a 2.5 solid to liquid ratio. The strength is increasing with the increasing solid to liquid ratio sample of geopolymer filler content.

Keyword: Geopolymer filler; fly ash; tensile; flexural; morphology; solid/liquid ratio

1. Introduction

Composite is composed of two or more materials to produce new material superior to individual constituents. The properties can be improved, such as compressive strength, tensile modulus, and impact strength. Composite also weight saving for its strength and stiffness [1-2].

Geopolymer is an amorphous network produced by mixing an alkaline activator and rich silicon aluminium materials such as fly ash, kaolin, and slag [3-6]. Geopolymer is also known as the type of inorganic polymer that can be formed at room temperature by using industrial waste or by-product to create a solid binder and having performed almost like Ordinary Portland cement (OPC) [7,8]. Geopolymer has a similar chemical composition with natural zeolite materials besides has an amorphous microstructure. A rapid chemical reaction under the alkaline condition on Si-Al minerals will result in a Si-O-Al and a three-dimensional polymeric chain based on the polymerization process [9].

Based on this project, the effect of different solid to liquid ratio of geopolymer filler for matrix resin for filament winding process has been observed. From the latest study by [10,11], geopolymer can be synthesized by using fly ash that contained high compressive strength, good fire resistance, and good acid resistance besides a low-cost material. Geopolymer also has an endothermic reaction that significantly influences curing time. Based on the study of fly ash-based geopolymer mortar [12], the increase in NaOH concentration (12-16 M) affected the growth of compressive strength. Sodium silicate solution also enhances the significant compressive strength of the mortar sample. The mortar sample with NaOH and Na_2SiO_3 has 40.42 MPa for maximum compressive strength after 28 days compared to NaOH only has 33.45 MPa. The combination of sodium hydroxide and sodium silicate may have led to 1.2 times more compressive strength than sodium hydroxide only. Heah et al. (2012) studied the effect of SiO_2/Al_2O_3, SiO_2/Na_2O, H_2O/Na_2O, and Al_2O_3/Na_2O molar ratios compressive strength

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of geopolymer [13]. The researcher found that the increasing molar ratio of Al_2O_3/Na_2O was influenced by the increasing solid to liquid ratio. The Na_2O from the alkali activator solution and Al_2O_3 come out from aluminosilicate. Every Al atom needed one Na atom to reach equilibrium based on geopolymer chemistry. Meanwhile, Yahya et al. (2015) investigated on effect of solids-to-liquids, Na_2SiO_3 to NaOH, and curing temperature on the palm oil boiler ash (Si + Ca) geopolymerisation system found that the optimum value of solid to liquid ratio which is 2.5 will produce the high strength [14].

In this paper, fly ash-based geopolymer was filled with conservative diglycidyl ether of bisphenol A (DGEBA) epoxy, which became one of the utmost present attention in thermoset-based clay. Meanwhile, it offers acceptable adhesion to the substrate, east of processing, low cost, and excellent chemical resistance for a wide range of applications. Limited research has been done with the thermoset resin filled with geopolymer filler by varying solid/liquid ratio of geopolymer filler and how this composite works for that condition on the strength development. Thus, the present work to address the effect of solid/liquid ratio on the mechanical and physical properties of the composites. The primary material that used in this study is thermoset resin, fly ash, and alkaline activator. Fly ash-based geopolymer is usually prepared by mixing fly ash with sodium hydroxide (NaOH), and sodium silicate (Na_2SiO_3) acts as an alkaline activator.

2. Experimental

2.1. Material selection

The epoxy resin used was Diglycidyl Ether of Bisphenol-A (DGEBA) supplied by Euro Pharma SdnBhd, and hardener Isophorone diamine (IPDA) was obtained from Dr. Rahmatullah Holdings. Epoxy DGEBA was chosen as thermoset resin in this study because of its versatility, such as excellent adhesion with a wide range of organic components, curing at a wide temperature range, low shrinkage. Moreover, this epoxy resin has good chemical and corrosion resistance, excellent electrical insulation properties, and high tensile, compressive and flexural strength leads to various applications [26]. An alkaline activator is used to induced the silicon and aluminium atoms in the geopolymer raw materials [15]. In this research, class F fly ash had been used, obtained from Sultan Azlan Shah Power Station in Manjung. The fly ash is rich in calcium oxide (CaO) content. It can be defined as finely divided mineral residue resulting from coal combustion by the electric generating plant. Fly ash consists of inorganic matter present in the coal that has been fused during coal combustion into spherical form. The combination of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) was used to create an alkaline activator for this research. Sodium hydroxide pellets, which have a purity of 97-99% was mixed with distilled water to produce 12 M NaOH.

2.2. Sample preparation

Preparation of Geopolymer Filler

Geopolymerization is a chemical reaction process between geopolymer raw material with the alkaline activator solution. In this research, 0.5-2.5:1 solid to liquid ratio was used as the parameter variation. The mixture needs to stir rapidly for a short period to avoid the mixture hardening without homogenously reacted. After the mixture was homogeneously mixed and reacted with each other, fly ash-based geopolymer was immediately poured and spread over a tray. The mixture was cured for 24 hours in the oven at 80°C.

After taking it out from the oven, the hardened geopolymer paste was crushed using the crusher machine and dry-blender machine until fly ash-based geopolymer is obtained in powder form. The powder form of fly ash-based geopolymer was sieved using the siever with 150 μm.

The smaller the fly ash-based geopolymer's size will give the more prominent the total surface area, which will directly increase the fly ash-based geopolymer filler rate in a composite system.

Preparation of Epoxy Filled with Fly Ash-based Geopolymer Filler

In this research, five different ratios have been prepared, as shown in Table 1. Epoxy geopolymer was prepared using a mechanical mixer according to the mix design of the epoxy geopolymer resin formulation in Table 2. Firstly, epoxy resin was mixed with geopolymer powder for about 2 hours to make it homogeneous and then mix with curing agent/hardener for about 5 minutes [16]. Mixed epoxy geopolymer resin is poured into the rubber mould into a shape for tensile and flexural testing before the resin is cured. The samples it then left in the rubber mould at the ambient temperature before taking out from the mould.

TABLE 1

Ratio of solid to liquid of geopolymer filler

Ratio	Fly Ash (g)	NaOH Solution (g)	Na_2SiO_3 Solution (g)
0.5	100	100	100
1.0	100	50	50
1.5	100	33.3	33.3
2.0	100	25	25
2.5	100	20	20

TABLE 2

Mix Design of Epoxy Geopolymer Resin

Material	Epoxy resin + Epoxy Hardener (%)	Geopolymer Filler (%)
Fly Ash	70	30

2.3. Physical and mechanical characterization

Several physical and mechanical tests have been done in this study: chemical composition characterization, gel time/curing time characterization, tensile strength test, flexural strength test, and morphology characterization to determine the properties of epoxy filled with fly ash-based geopolymer. These tests were done after the curing process.

Elemental Composition Characterization

Fly ash was characterized by X-ray fluorescence (XRF) using (XRF-Qualitax, Italy). XRF analysis was conducted at the School of Materials Engineering, University of Malaysia Perlis (UniMAP), Perlis, Malaysia, to identify the chemical composition of the raw material fly ash.

Gel Time/Curing Time Characterization

The gel time is tested according to ASTM D3532 standard. The gel time is when cross-linking extends throughout a reacting resin system, evident as a sudden inability to flow. The gelation of epoxy/fly ash-based geopolymer was prepreg by a rheometer machine with a heating rate of 2.5°C/ min. The time from the heat application until the resin stops forming strings by contact with the pick is referred to as gel time.

Tensile Strength Test

Fig. 1 illustrates the tensile strength test conducted according to ASTM D638 standard using Universal Testing Machine (UTM) Instron's 3400 Series with 50 kN force transducer. There are 15 samples with five different solid to liquid ratio of fly ash-based geopolymer. The specimen size test is 5 mm × 15 mm × 132 mm.

Flexural Strength Test

Using ASTM D790, a flexural test was performed using Universal Testing Machine (UTM) Instron's 3400 Series with 50 kN force transducer. The test procedure used was a three-point loading system using center loading. The cross-speed and

Fig. 1. The Illustration of Tensile Test

span lengths were set to 5 mm/min and 50 mm, respectively. The cured resin was rectangular in size 5 mm thickness, 15 mm width, and 132 mm. This testing contributed to the three-point bending that showed in Fig. 2.
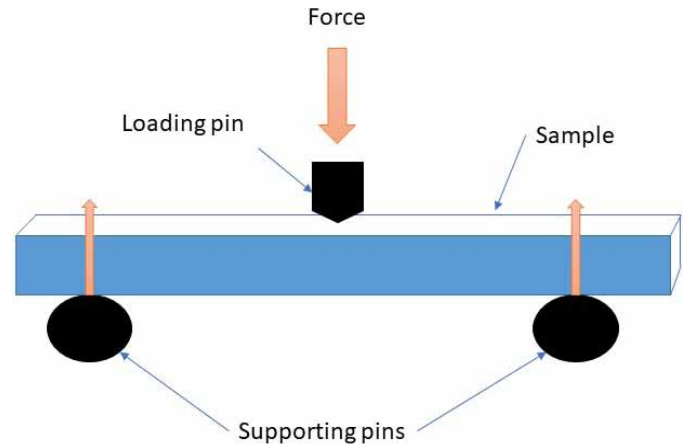

Fig. 2. The Illustration of Flexural Test

Morphology Characterization

A scanning electron microscope (JEOL Ltd., Japan) was used to analyse fly ash-based geopolymer, and fracture surface of epoxy filled with fly ash-based geopolymer. All samples were coated before undergoing SEM to enhance conductivity and tested at an accelerating voltage of 10-20 kv.

3. Results and discussion

3.1. Chemical composition analysis

Table 3 shows the chemical composition of fly ash raw material obtained from X-ray fluorescence (XRF). The main chemical composition of fly ash is silicon oxide SiO_2, followed by Fe_2O_3, CaO, and Al_2O_3.

TABLE 3

Material composition of raw fly ash

Compound	Mass (wt. %)
SiO_2	55.90
Al_2O_3	27.80
Fe_2O_3	7.09
CaO	3.95
TiO_2	2.25
K_2O	1.55
SrO	0.37
SO_3	0.33
RuO_2	0.24
ZrO_2	0.13
V_2O_5	0.10
MnO	0.06
CuO	0.05

Raw material fly ash can be classified as Class F based on the data given, referred to as ASTM C618, where the calcium content (3.95%) is less than 20%. The summation of SiO_2 and Al_2O_3 is 83.7%, which is the essential composition to create a respectable geopolymer [17,18]. The adequate CaO in the fly ash-based geopolymer mixture is also reported as a suitable source to produce a geopolymer that can be cured at room temperature [19].

3.2. Gel time/curing time analysis

Based on Fig. 3, it is clearly showing that gel time/curing time gradually decreases with the increase of the solid/liquid ratio. This can be related to the less water available in the epoxy/geopolymer as the solid/liquid ratio increased, resulting in faster hardening of the gel phase.
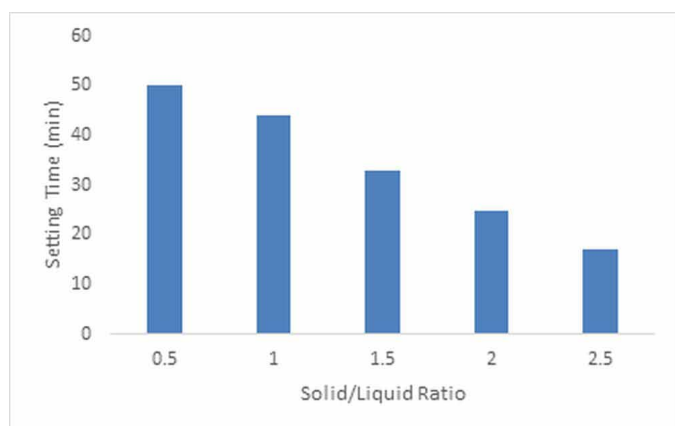
Fig. 3. Setting Time vs Solid/Liquid ratio

When the smaller the solid/liquid ratio is, the longer the initial setting time is. However, when the higher the solid/liquid ratio is, the shorter the initial setting time is. The setting time or gel time is related to the degree of polymerization [27]. Na^+ exists as a hydrated ion in an aqueous solution. When the solid/liquid ratio is heightened or boosted with the higher concentration of activator, a large amount of water and Na^+ are required to form a hydrated state, resulting in the rapid reduction of free water and a shorter setting time. The solid/liquid ratio influences the setting time of the epoxy/geopolymer filler.

3.3. Tensile strength analysis

Based on Fig. 4, the lowest tensile strength is 3.09 MPa, which is a solid to liquid ratio of 0.5. It contributed to the intense strength of geopolymer paste due to a high alkaline activator content. The alkaline activator's high content produced excessive OH^- left in the system, thus weakening the geopolymer structure [21].

From Fig. 4 also, the sample with a 2.0 solid to liquid ratio is the highest tensile strength with 10.06 MPa. The increase in
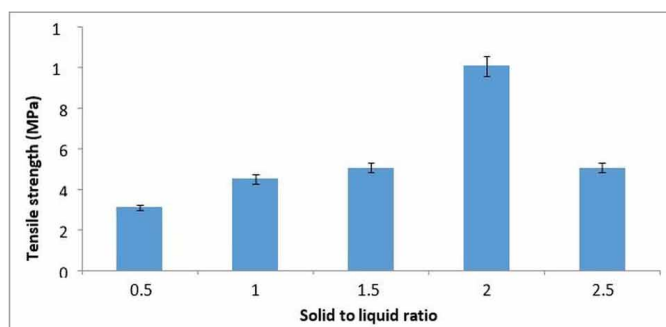
Fig. 4. Tensile Strength of Fly Ash-Based Geopolymer at Different Solid to Liquid Ratio

the tensile strength due to an increase in the ratio, respectively. This result proved additives' capability to enhance adhesion and improve tensile strength properties. The increase of the ratio helped enhance the interaction between the filler of interfacial de-bonding and improved the properties. Thus, strong adhesion between the filler and matrix interface can cause better stress transfer from the matrix to the filler, leading to a higher tensile strength [18].

However, in the sample with a 2.5 solid to liquid ratio, the tensile strength showed decreasing with a value of 5.06 MPa. As the solid to liquid ratio increased, thus increasing the interfacial area, the deteriorating interfacial bonding between filler (hydrophilic) and matrix (hydrophobic) reduced the tensile strength. For irregularly shape fillers, the composites' strength decreases due to the filler's inability to support stresses transferred from the polymer matrix. Simultaneously, poor interfacial bonding sources incompletely separated micro-spaces between filler and matrix polymer, impeding stress propagation when tensile stress is loaded and encourages increased brittleness [19].

3.4. Flexural strength analysis

Typical graphs from the flexural strength tests for epoxy filled with geopolymer solid to liquid ratio 0.5-2.5 are shown in Fig. 5. Generally, all entire specimens failed after the flexural stress reached the maximum value.

From Fig. 5, a sample with a 0.5 solid to liquid ratio shows the lowest flexural strength, which is 2.18 MPa, while the sample with a 2.0 solid to liquid ratio shows the highest flexural strength, which is 3.05 MPa. The result revealed that the fly ash ratio's addition generally yields a better result in flexural behavior. The excessive liquid may lead to a low geopolymerization process because of the effect of the fly ash's expected reaction as a filler to the matrix. The most insufficient flexural strength might also be due to an excess of OH^- concentration [22]. The increasing solid/liquid ratio led to the development of the fly ash-based geopolymer's flexural performance. This ratio is the optimum ratio for the fly ash-based geopolymer compared to the other ratio [23,24].

The increase in strength observed with a high amount of fly ash can be explained by considering the introduction of a material
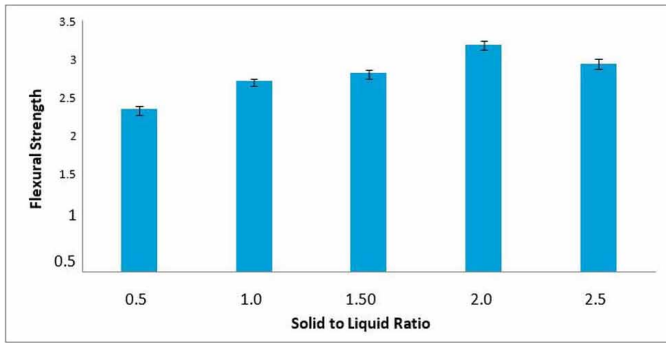
Fig. 5. Flexural Strength of Fly Ash-Based Geopolymer at Different Solid to Liquid Ratio

with higher compressive strength than the geopolymer matrix and reducing the microcracking related to the drying shrinkage of the binder phase [13]. It is well known that aggregate properties strongly affect geopolymer drying shrinkage behaviour [25]. As shown in Fig. 5 shows the decreasing flexural strength when the solid to liquid ratio reaches 2.5, which is the sample's flexural strength, which is only 2.81 MPa. This is due to the smaller agglomerated and disordered nature of clay and the uses of lower molarity of NaOH [22].

3.5. Morphologyanalysis

In this research, fly ash Class F had been used as source material in fly ash-based geopolymer. Low-calcium (ASTM Class F) fly ash is preferred as source material than high-calcium (ASTM Class C) fly ash. The presence of calcium in high amounts may interfere with the polymerization process and alter the microstructure [20]. Class F fly ash generated from the burning anthracite or bituminous has a low calcium content and has a total SiO_2, Al_2O_3, and Fe_2O_3 range over 70 wt%, while CaO content less than 10% [1]. The morphology structure of the fly ash had been shown in Fig. 6.

Fig. 6 showed that the samples' microstructure images are mostly composed of small and spherical particles. The smooth
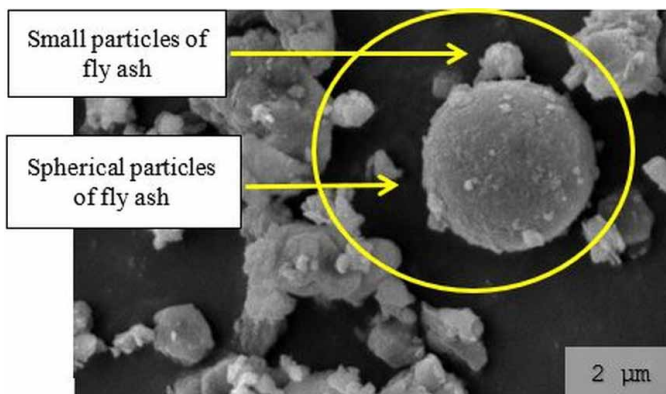

Fig. 6. Fly ash undergo Scanning Electron Microscope up 8000× magnification

aluminosilicate spherical particles are formed due to the thermochemical transformations of mineral particles during the coal combustion process. The minerals melt to form tiny droplets, which upon sudden cooling and action of surface tension forces, adopt the spherical shape.

As shown in Fig. 7, the higher composition of fly ash is Si, O, and Al. There are reactions between fly ash and alkali and condensation between the resultant Si^{4+} and Al^{3+} species, followed by other complex nucleation, oligomerization, and polymerization, leading to a new aluminosilicate-based polymer with a new amorphous three-dimensional network structure. The critical role in the formation geopolymerization is thought to be played by alkali activation on fly ash: in an alkaline solution, the silica, the alumina, or the aluminosilicates in fly ash hydrolyze, -Si-O-Si- or -Si-O-Al- bonds of aluminosilicate break and release active Al^{3+} and Si^{4+} species [20].
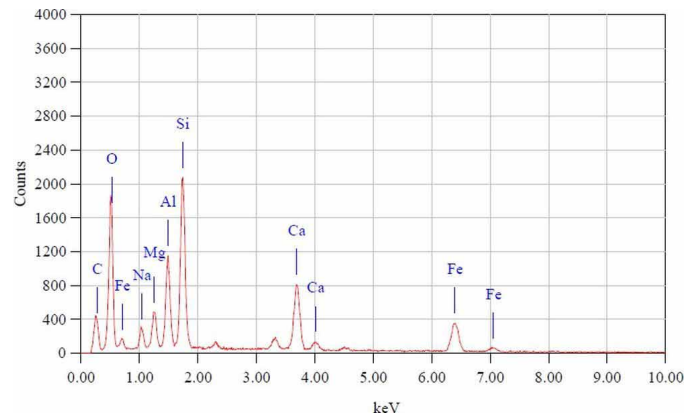

Fig. 7. Fly Ash Spectrum and Content of Individual Elements

The SEM micrograph of tensile fracture of epoxy and epoxy filled with fly ash-based geopolymer was shown in Fig. 8a and Fig. 8b. As shown in Figure 8a, a smooth fracture surface is observed on an epoxy resin that specified relatively brittle fracture. While Fig. 8b illustrates the SEM images of epoxy filled with fly ash-based geopolymer where the bright topographies correspond to fly ash-based geopolymer filler with good dispersal. It is well known that if the Young Modulus of second phase particles is lower than the matrix, the particle turns as a stress concentrator in particulate-filled polymer systems.

4. Conclusion

The study of the effect of different solid to liquid ratio on epoxy filled with fly ash-based geopolymer was managed. The impact of the solid to liquid ratio was studied in terms of physical and mechanical properties. From the research, the solid to liquid ratio that gives the best mechanical properties is 2.0. This research shows that epoxy filled with fly ash-based geopolymer was developed based on a different solid to liquid ratio of the geopolymer material. The microstructure of the composites is smoother and denser, with fewer unreacted fly ash particles and
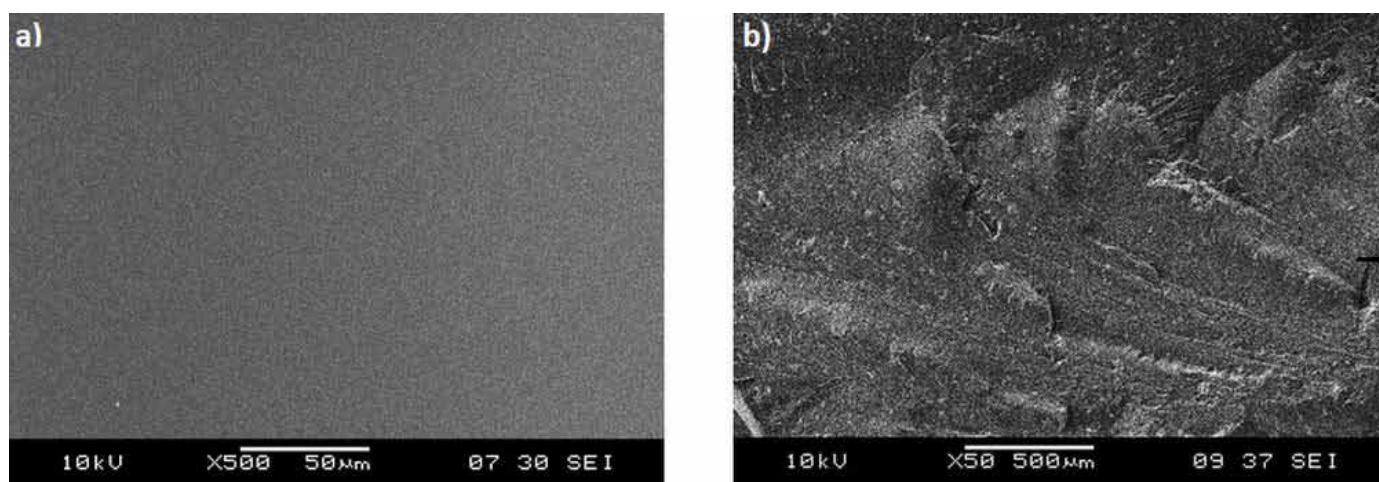
Fig. 8. SEM images of (a) DGEBA epoxy resin, (b) epoxy filled with fly ash-based geopolymer at 50× magnification

pores. It was shown that the content of the alkaline activator solution is the most crucial parameter affecting the strength of epoxy filled with fly ash-based geopolymers. The waste material-based geopolymer's functional properties have a more significant potential to be an ideal replacement matrix of composite with glass fiber in the filament winding technique.

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